

Novel One Step Sonosynthesis and Deposition Technique to Prepare Silver Nanoparticles Coated Cotton Textile with Antibacterial Properties

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Abstract—In this work, a novel, fast and one step sonochemical synthesis and deposition technique to prepare silver nanoparticles (AgNPs) coated cotton fabrics is developed. The reaction medium consisted of silver nitrate, hexamethylenetetramine as reducing agent and polyvinylpyrrolidone as the polymeric stabilizer. The AgNPs-deposited cotton fabrics were characterized by UV-visible spectroscopy, X-ray diffraction, attenuated total reflectance Fourier transform infrared spectroscopy, dynamic light scattering and scanning electron microscopy techniques. The hydrodynamic diameters of the particles were found to increase from 32 to 144 nm with increase in the irradiation time from 30 to 90 min. Electron micrographs of the AgNPs deposited cotton fabrics showed uniform deposition of the particles on cotton. The AgNPs-deposited cotton fabrics showed excellent antibacterial activities against Gram-negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*) and moderate antimicrobial activities against Gram-positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*).

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INTRODUCTION

Textiles with antimicrobial properties are the need of time to improve personal hygiene and to prevent bacterial infections [1, 2]. Different pathogenic bacteria can easily survive on various textiles like cotton as it supports the growth of microorganisms such as bacteria and fungi [3]. The growth of microbes on textiles during its use and storage can cause serious hygiene issues [4]. Antibacterial textiles are prepared by the deposition or coating of antibacterial nanomaterials on them [4, 5]. In the last decade, some significant developments were observed in the preparation of antibacterial nanotextiles by this approach [6, 7]. In particular, silver nanoparticles (AgNPs) have been extensively used for the preparation of antibacterial nanotextiles because of their very high antimicrobial, antifungal and antioxidant activities [8, 9]. The deposition of AgNPs on cellulose fibers in cotton can be achieved by various techniques such as in situ or post-synthesis deposition, padding and dry cure technique etc. The sonochemical method has been found to be the most effective for the deposition of AgNPs on textiles [10–13].

There are several reports about the synthesis of various silver nanostructures by sonochemical methods [14, 15]. Although silver nanostructures can be synthesized easily, their post-synthesis deposition on textiles is difficult. Hence, even after many attempts of the deposition of AgNPs on textiles, none of the techniques has reached final stages of technological readiness level. Further, the in situ synthesis and deposition of AgNPs on textiles followed by a detailed study of their size-dependent antimicrobial property is lacking in the literature.

For this purpose, in the this work we have developed a novel, one step and fast sonosynthesis and deposition technique to prepare AgNPs coated cotton fabrics with antibacterial properties. The synthesis conditions involved silver nitrate as the precursor, hexamethylenetetramine (HMTA) as the reducing agent and a water soluble polymer polyvinyl pyrrolidone (PVP) as the stabilizing agent for the nanoparticles. The size of nanoparticles was tuned by varying the irradiation time during the sonochemical synthesis and deposition. The AgNPs-deposited cotton fabrics were studied for their size-dependent antimicrobial activity against various Gram-positive and Gram-

negative bacteria. The method of sonosynthesis and in situ deposition of AgNPs on cotton developed in this work can be easily adapted in an industrial set up to produce cotton fabrics with antimicrobial properties.

EXPERIMENTAL

Materials

Silver nitrate (assay $\geq 99.0\%$), HMTA and PVP (molecular weight 40000) were purchased from Sigma-Aldrich and they were of analytical pure grade. The reagents were used as received. Double deionized water was used for all experiments. Untreated cotton fabric was supplied by Dattajirao Kadam Technical Education (DKTE) Society, Ichalkaranji, Maharashtra India's textile engineering division.

The pathogens *Escherichia coli* (NCIM 2832), *Staphylococcus aureus* (NCIM 2654), *Pseudomonas aeruginosa* (NCIM 5032) and *Bacillus subtilis* (NCIM 2635) used for the antimicrobial activity were collected from Department of Microbiology, Shivaji University Kolhapur, Maharashtra, India.

Methods and Instruments

An ultrasonic probe sonicator from PCI Analytics (Ti-horn diameter 8 mm, frequency 20 kHz and power 250 W) was used for the sonochemical synthesis of AgNPs and their in-situ deposition on the cellulose fibers in cotton.

The UV-visible spectra were registered on Cary-60 spectrophotometer. The X-ray diffraction (XRD) patterns of the AgNPs were registered on Bruker D2 Phaser diffractometer using 5 s/scan speed. The 2θ value ranged from 20° – 80° with $\text{CuK}\alpha$ radiation (1.5405 Å, 30 kV, 10 mA). The average crystallite size of the synthesized AgNPs was calculated by using Debye–Scherrer formula.

The hydrodynamic diameters of AgNPs were measured using particle analyzer NanoPlus (Particulate Systems, USA). The 0.1 w/v suspensions of the particles were prepared and sonicated for at least 30 min before the analysis.

The surface morphology of AgNPs-deposited cotton fabrics was analyzed by JEOL JSM-6360 scanning electron microscope (SEM) at an acceleration voltage of 20 kV. Before the SEM analysis, the samples were sputter-coated with gold.

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded with Perkin Elmer spectrometer operated at room temperature ($25 \pm 1^\circ\text{C}$) with nominal resolution of the detector of 2 cm^{-1} . An advanced ATR baseline correction was applied to all spectra in the range of 4000 to 600 cm^{-1} .

Disk diffusion method was used to check the antimicrobial activity of AgNPs deposited cotton fabrics against Gram-positive and Gram-negative bacteria.

Synthesis and Deposition of AgNPs on Cotton Fabric

The in-situ synthesis and deposition of AgNPs on cotton fabric by sonochemical method was carried out as follows. AgNO_3 (0.085 g), HMTA (0.04 g), and PVP (0.020 g) were dissolved in 50 mL double distilled water and sonicated by using probe sonicator at different irradiation time in the presence of $3\text{ cm} \times 3\text{ cm}$ cotton fabric sample. The reduction was carried out at three different irradiation times, i.e. at 30, 60 and 90 min, which corresponds to the sample codes H1, H2, and H3, respectively. The reaction temperatures recorded for samples H1, H2 and H3 were equal to 40, 49 and 57°C correspondingly. At the end of the reaction, the color of the fabric changed from white to light brown with varying intensity depending upon the irradiation time. The AgNPs deposited cotton fabrics were first washed thoroughly with water to remove traces of reducing and stabilizing agents and then with ethanol. The fabrics were dried overnight at 65°C in the oven.

RESULTS AND DISCUSSION

Sonosynthesis and Deposition of AgNPs

The sonochemical synthesis of AgNPs and their in-situ deposition on cotton fabrics was carried out at different irradiation times. The overall scheme of the work is shown in Fig. 1.

HMTA is well-known mild reducing agent which serves for the reduction of Ag^+ ions to AgNPs. The reduction of metal ions (Ag^+ to Ag^0) is possible by both ultrasound waves and HMTA. During the sonosynthesis of AgNPs, HMTA acts as a reducing agent and the ultrasound-generated $\cdot\text{H}$ and $\cdot\text{OH}$ radicals are also responsible for the reduction. But the rate of reduction induced by $\cdot\text{H}$ and $\cdot\text{OH}$ radicals is low as compared to the rate of reduction by HMTA. So, the ultrasound waves mostly assist in deposition of NPs on the textile substrate. The PVP provides nucleation sites for the nanoparticles by complexing the Ag^+ ions (at C=O group) and it also form a stabilizing and protective layer around the particles immediately after their formation. The irradiation time was varied purposely to study its effect on particle size as well as on the antimicrobial activity of the final product. The antibacterial activity of metal and metal oxide nanoparticles depends upon size, shape and concentration. As size decreases the surface area to volume ratio of nanoparticles increases which leads to an increase in the antibacterial activity of the AgNPs [20]. Therefore, the goal of this work was to achieve uniform deposition of very small AgNPs with narrow particle size distribution on cotton substrate.

The sonochemical synthesis and deposition process involves the rapid formation and immediate deposition of AgNPs on cotton in a single step [15]. The AgNPs produced are bombarded on the surface of the cotton yarns by very high energy sonochemical

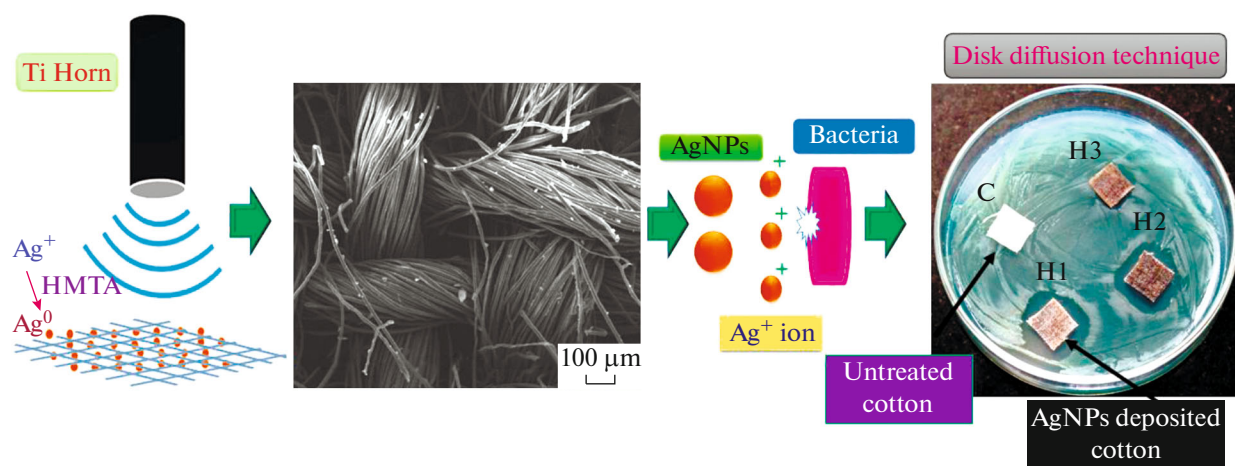


Fig. 1. Overall scheme of the work.

microjets resulting from the collapse of the sonochemical bubbles. The extreme conditions created during the sonosynthesis using probe sonicator guarantees the formation and fast and simultaneous deposition of AgNPs on the textile [16–18]. Although this process mainly results in physical adsorption of the nanoparticles on the cellulose fibers in cotton, the hydroxyl groups on cotton through hydrogen bonding network and cavities in the cellulose fibers hold the particles tightly on the fibers [6]. The nanoparticle size increases with increasing irradiation time, as the primary particles (seeds) formed grow in size with continuous reduction of Ag^+ ions on their surface [19]. During the in-situ synthesis and deposition, the ultrasonic waves accelerate the transport of newly generated AgNPs to the cotton fabric surface. This effect is higher at longer irradiation times [20].

UV-Visible Spectroscopy

The Fig. 2 shows the UV-visible spectra of colloidal suspensions of the sonosynthesized AgNPs at different irradiation times in the range from 200–800 nm. The formation of AgNPs was visible by the change in color of the silver nitrate solution. The intensity (in the form of absorbance value) of the peak due to surface plasmon resonance (SPR) around 437 nm found to be increasing with increase in the irradiation time [21]. A slight red-shift of the SPR band from 437 to 442 nm was observed which indicated the increase in size of particles with increase in irradiation time. This increase in size was further confirmed by DLS and XRD analyses.

X-ray Diffraction

The crystalline state and crystallite size of the AgNPs were confirmed by registering the XRD patterns of the samples in the 2θ range of 10° – 80° . The

Fig. 3 shows the XRD patterns of untreated or pristine cotton fabric (C) and AgNPs-deposited cotton fabric samples for different irradiation times (H1, H2, and H3). The XRD patterns demonstrate that the AgNPs are crystalline in nature and the diffraction peaks match to the face centered cubic phase of AgNPs (JCPDS card No. 01-087-0717) [22]. The peaks at $2\theta = 38.03^\circ$, 44.23° , 64.39° and 77.32° are assigned to the (111), (200), (220) and (311) reflection lines of cubic Ag particles, respectively [13]. The sample C (pristine cotton) shows two peaks at 22.45° and 25.41° probably coming from the crystalline part of the cellulose in the fibers [23]. The average crystallite size estimated by the Debye–Scherrer equation is 10, 31 and 64 nm for samples H1, H2 and H3, respectively [25].

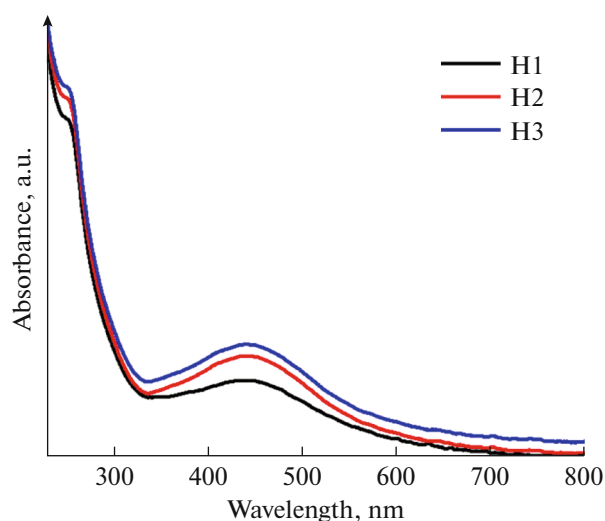


Fig. 2. UV-visible spectra of AgNPs sonosynthesized at irradiation times of (H1) 30, (H2) 60, and (H3) 90 min, respectively.

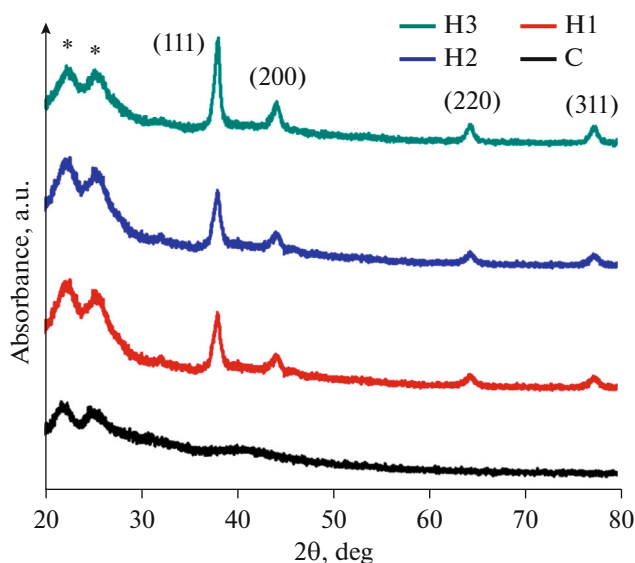


Fig. 3. XRD patterns of (C) pristine cotton and AgNPs-deposited cotton fabrics prepared at irradiation times of (H1) 30, (H2) 60 and (H3) 90 min, respectively.

The XRD results clearly confirmed the crystalline state of AgNPs and their presence on the cotton fabric samples. The hydrodynamic diameter of the particles was found to be increased from 32 to 144 nm with increase in the irradiation time from 30 to 90 min. The results of UV-visible spectroscopy, XRD and DLS are summarized in Table 1.

ATR-IR Spectroscopy

The deposition of the AgNPs on cotton was further confirmed by registering the ATR-IR spectra of the pristine and AgNPs-deposited cotton fabrics prepared at different irradiation times (Fig. 4). However, the cotton fabric (cellulose) peaks were predominant over other peaks. The broad peaks in the regions of 3000 cm^{-1} and 3400 cm^{-1} were due to the adsorbed water and hydroxyl groups of cellulose. The typical absorption peak of PVP at around 1660 cm^{-1} was clearly visible which is present also in all the AgNPs-deposited cotton fabric samples [24]. This confirms that the PVP acts as a stabilizer for the nanoparticles and forms a reasonably stable coating around the particles which remain intact during and after the deposition. This PVP layer may enhance the interactions of $-\text{OH}$

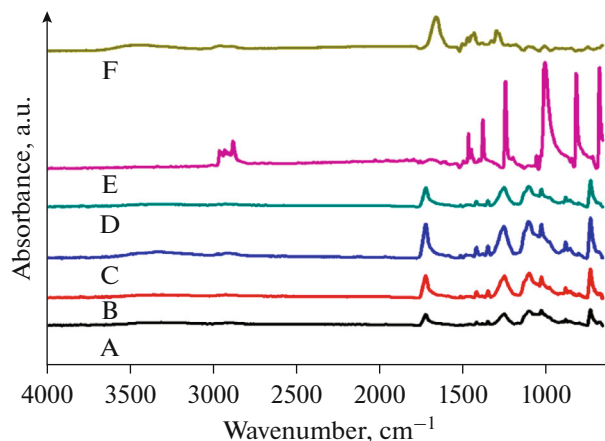


Fig. 4. ATR-FTIR spectra of (A) pristine cotton, samples (B) H1, (C) H2, and (D) H3; and (E) HMTA and (F) PVP.

groups from cellulose with the groups such as carbonyl ($\text{C}=\text{O}$) and $-\text{N}$ (with lone pair) present on the PVP chains [26]. These interactions further increase the stability of the particle coating.

Scanning Electron Microscopy

The SEM images of the AgNPs-deposited cotton fabrics at different magnifications are shown in Fig. 5. The deposition of AgNPs on cotton yarns at different irradiation times can be clearly seen. The magnified images showed deposition of single particles and also clusters made of primary particles on the yarns. An increased deposition of the particles was observed with increase in the irradiation time but on the other hand the size of the nanoparticles grows as the irradiation time is increased.

The Fig. 6 shows the photographs of the AgNPs-deposited cotton fabrics prepared at various irradiation times. In the photographs, change in intensity of the color of fabric with increase in the deposition can be clearly seen. Thus, deposition of the AgNPs on cotton fabrics analyzed by the XRD and IR spectroscopy methods was further confirmed with the SEM images.

Antimicrobial Activity

The antibacterial properties of AgNPs deposited cotton fabrics were checked against both Gram-positive and Gram-negative bacteria using the disk diffu-

Table 1. Results of DLS, UV-visible and XRD analyses of AgNPs obtained by sonochemical method

| Sample code | Concentration of AgNO_3 , mM | Volume, mL | Irradiation time, min | Hydrodynamic diameter ± 8 nm | λ_{SPR} , nm | Average crystallite size, nm |
|-------------|---------------------------------------|------------|-----------------------|----------------------------------|-----------------------------|------------------------------|
| H1 | 10 | 50 | 30 | 32 | 437 | 10 |
| H2 | 10 | 50 | 60 | 64 | 439 | 31 |
| H3 | 10 | 50 | 90 | 144 | 442 | 64 |

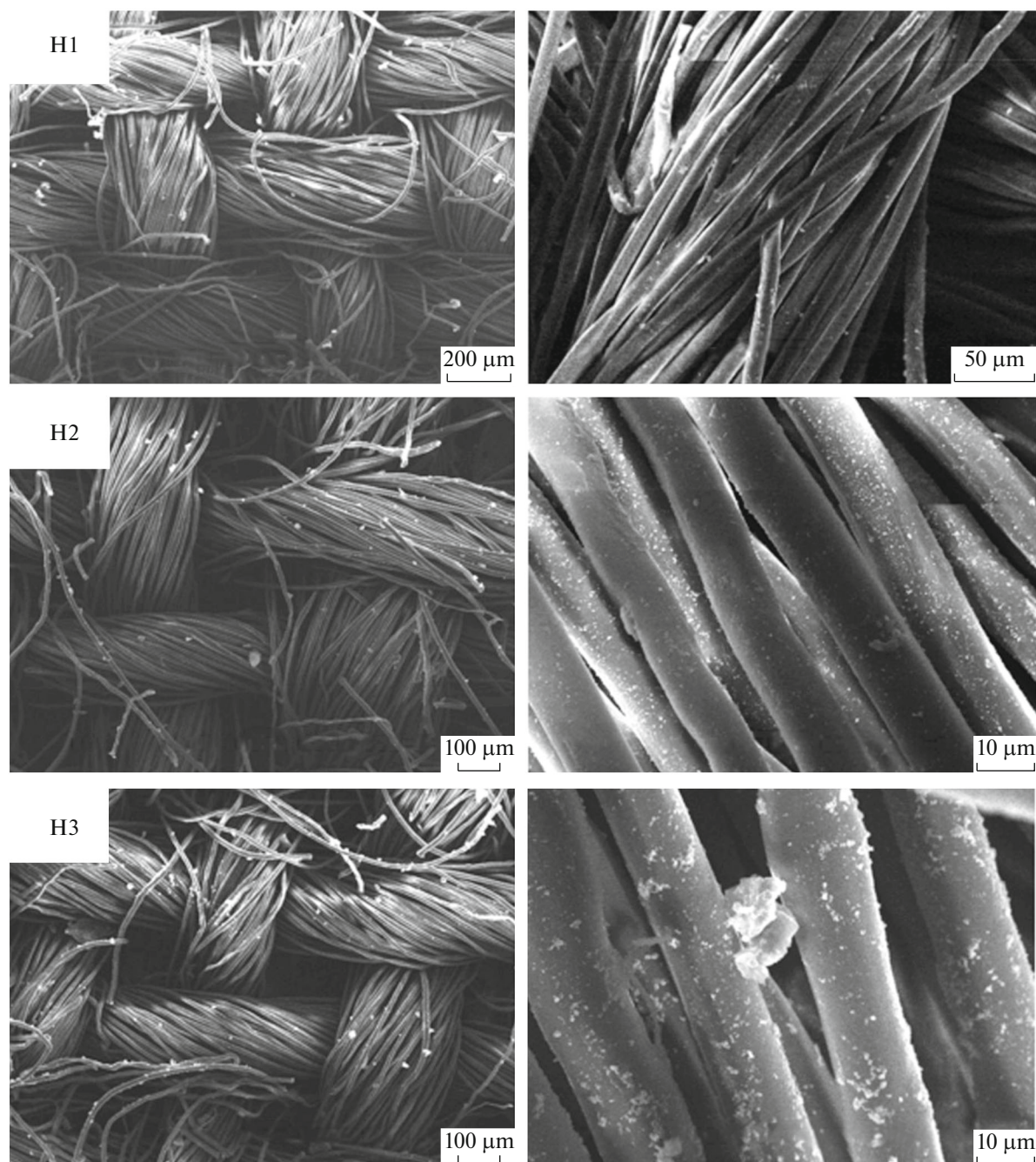


Fig. 5. SEM images of AgNPs-deposited fabrics prepared at irradiation times of (H1) 30, (H2) 60, and (H3) 90 min, respectively.

sion technique. The bacteria used were *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Bacillus subtilis*. The pristine (before deposition) cotton fabric was used as a control (reference). The Fig. 7 shows the results of the antimicrobial activity of pristine and AgNPs deposited cotton fabrics prepared at different irradiation times (H1, H2 and H3 samples). The control samples did not show any zone of inhibition and growth of the bacteria was observed on or near the fabric. The AgNPs-deposited cotton fab-

rics showed excellent antibacterial activities against Gram-negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*) and moderate antimicrobial activities against Gram-positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*).

The antimicrobial activity was enhanced significantly as the particle size reduced from 144 to 32 nm. The highest zones of inhibition (up to 28 mm) were shown by the particles obtained with short (30 min) irradiation time and smallest in size. This is due to the

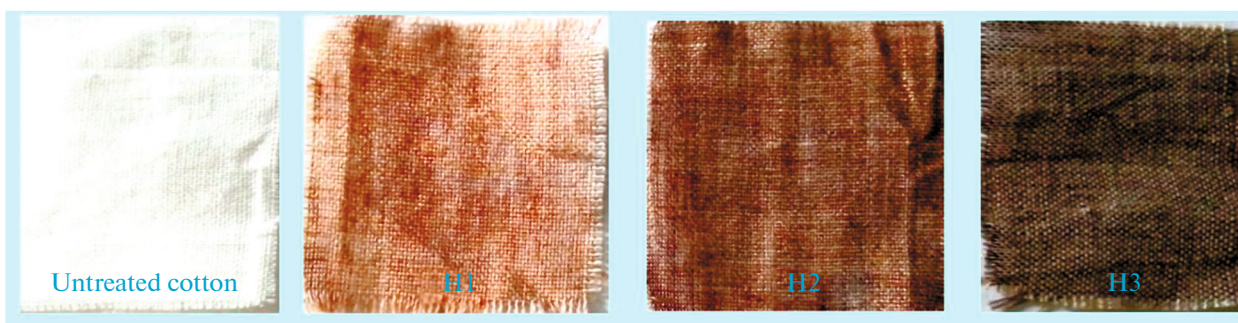


Fig. 6. Photos of the untreated cotton fabric and AgNPs-deposited fabrics prepared at irradiation times of (H1) 30, (H2) 60 and (H3) 90 min, respectively.

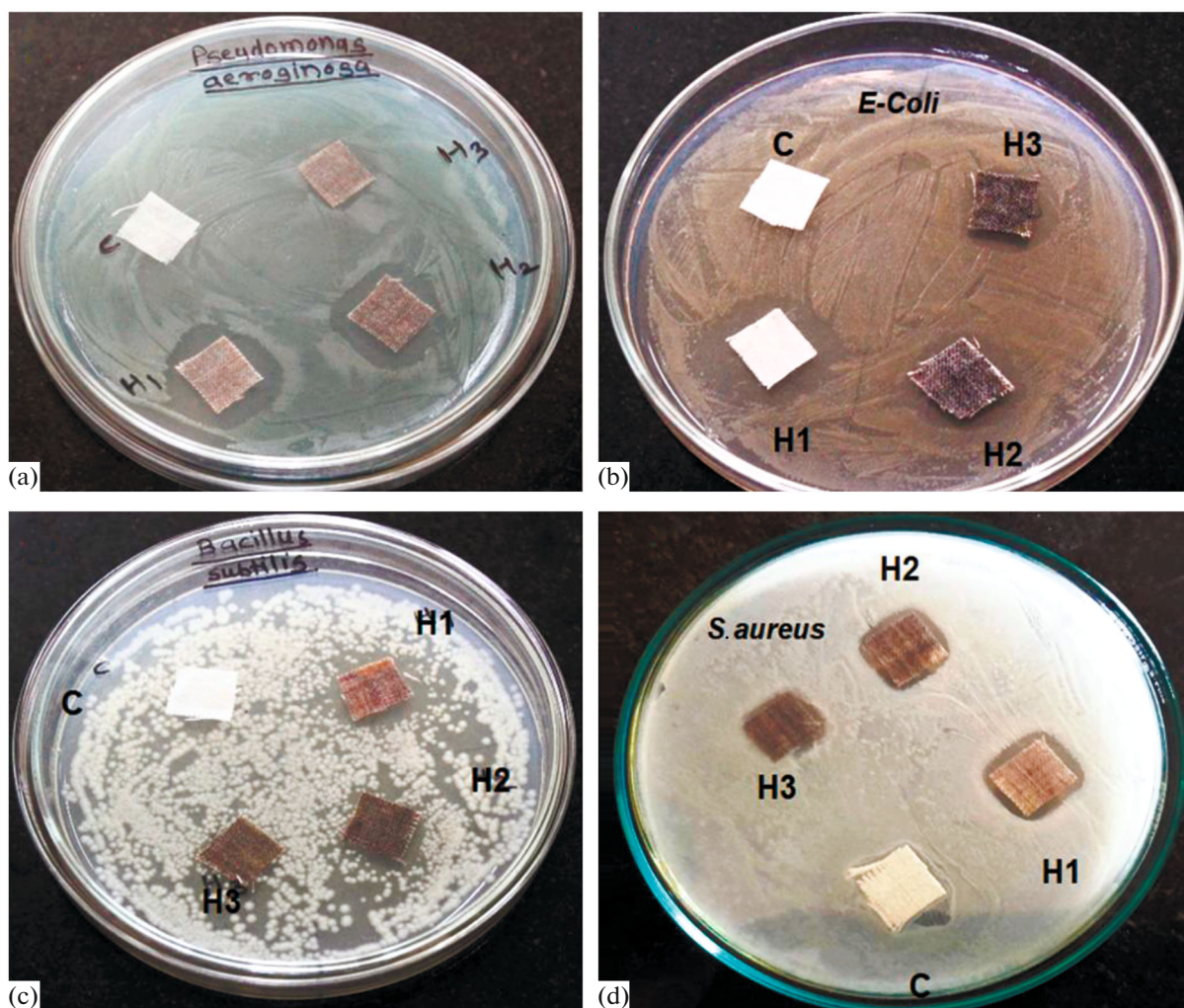


Fig. 7. Antimicrobial activity of AgNPs-deposited cotton fabrics prepared at different irradiation times (samples H1–H3) against (a) *Pseudomonas aeruginosa*, (b) *Escherichia coli*, (c) *Bacillus subtilis*, and (d) *Staphylococcus aureus*.

very high surface area of the small size AgNPs [26]. The small nanoparticles can get easily attached to the bacterial cell membrane and enter inside the cell and accumulate there. The AgNPs release silver ions by the

process of slow oxidative dissolution causing major damage to the nuclei resulting in the death of bacteria [23, 27, 28]. The higher zones of inhibition for all types of bacteria were observed for AgNPs-deposited cotton

Table 2. Antimicrobial activity of AgNPs deposited cotton fabric

| Sample code | Hydrodynamic diameter \pm 8 nm | Zone cleared by AgNPs deposited fabric, mm | | | |
|-------------|----------------------------------|--|-------------------------------|--------------------------|------------------------------|
| | | <i>Escherichia coli</i> | <i>Pseudomonas aeruginosa</i> | <i>Bacillus subtilis</i> | <i>Staphylococcus aureus</i> |
| H1 | 40 | 28 | 22 | 20 | 15 |
| H2 | 64 | 20 | 21 | 15 | 13 |
| H3 | 144 | 18 | 13 | 11 | 11 |

samples prepared with the short (30 min) irradiation time. The results of the antimicrobial activity of all samples together with the sizes of AgNPs are reported in Table 2. The antimicrobial activity by the AgNPs-deposited cotton fabrics was higher against the Gram-negative bacteria in comparison with Gram-positive bacteria, this may be because of the higher peptidoglycan concentration in Gram-positive bacteria than the Gram-negative bacteria which resist the action of NPs [29]. In addition, this difference in activity could be due to the difference between the cell wall structure of bacterial strains. The outer membrane in Gram-positive bacterial cell wall possess more complex structure and restricts entry of the several substrates/compounds including nanoparticles across it [30].

CONCLUSION

In this work, a single step, efficient and cost effective sonochemical technique is developed to prepare AgNPs deposited cotton fabrics with antimicrobial properties. The results of UV-visible, XRD, DLS, ATR-FTIR, and SEM analyses revealed the formation of stable and monodispersed AgNPs and their uniform deposition on the cotton fabrics. The XRD analyses indicated that the AgNPs deposited on cotton fabric were cubic shaped and crystalline in nature. The DLS results showed an increase in the particles size with increasing ultrasound irradiation time. The antimicrobial activity of AgNPs deposited cotton fabrics revealed that the smaller size particles obtained with short (30 min) irradiation time show highest antimicrobial activity. Due to the simplicity, efficiency and industrial feasibility of the technique developed in this work, it can be potentially transferred in to textile production industries with minimum modification of the present technology.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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